

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 14/06, 36/04, C08J 9/04	A1	(11) International Publication Number: WO 99/47573 (43) International Publication Date: 23 September 1999 (23.09.99)
(21) International Application Number: PCT/US99/05945 (22) International Filing Date: 18 March 1999 (18.03.99) (30) Priority Data: 60/078,470 18 March 1998 (18.03.98) US (71) Applicant (for all designated States except US): WORLD PROPERTIES INC. [US/US]; Suite 410, 7366 North Lincoln Avenue, Lincolnwood, IL 60646 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BESSETTE, Michael, D. [US/US]; 416 Chaffeeville Road, Storrs, CT 06268 (US). SETHUMADHAVAN, Murali [IN/US]; 12 Redcoat Road, Framingham, MA 01701 (US). (74) Agent: REIMER, Leah, M.; Cantor Colburn LLP, 88 Day Hill Road, Windsor, CT 06095 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW. ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MICROCELLULAR THERMOPLASTIC ELASTOMER FOAMS AND METHOD OF MANUFACTURE THEREOF (57) Abstract <p>A low density, microcellular thermoplastic elastomeric foam is presented, wherein the foam has closed cells. The foam is manufactured using supercritical fluid as the blowing agent, wherein the pressure drop rate across the die is in the range from about 0.1 to about 4.8 GPa, and the melt temperature of the resin composition is in the range from about 320–360 °C.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

MICROCELLULAR THERMOPLASTIC ELASTOMER FOAMS AND METHOD OF MANUFACTURE THEREOF

Background of the Invention

1. Field of the Invention

This invention relates generally to the field of thermoplastic elastomers. More particularly, this invention relates to microcellular thermoplastic elastomers foamed
5 using supercritical fluids.

2. Description of the Related Art

Thermoplastic elastomers have a wide range of uses, particularly as foams. Foamed thermoplastic elastomers have found utility as shock absorbing components for equipment casings, automobiles and footwear, as well as in medical applications.
10 Despite their popularity, presently available thermoplastic elastomeric foams suffer from various drawbacks and limitations. For example, they are manufactured primarily as open-celled foams, which limits their usefulness in sealing applications. Commonly-used manufacturing processes, requiring chemical or mechanical foaming, are expensive, and yield foams with inherent density limitations. Foams are also not
15 available in the form of thin sheets, i.e., sheets of less than about 50, and preferably less than about 15 mils.

-2-

Accordingly, there remains a need in the art for foamed thermoplastic elastomers in the form of thin sheets, that have closed cells and lower densities of less than about 20 lbs/ft³ (pcf), and that are manufactured by economical processes.

Summary of the Invention

5 The above-described and other problems and deficiencies of the prior art are overcome or alleviated by the present foamed thermoplastic elastomers and method for manufacturing the same, wherein a thermoplastic elastomer resin is foamed using a supercritical fluid under conditions of controlled temperature and pressure drop rate, thereby producing closed-cell, microcellular foams. Such foams may be produced in
10 the form of thin sheets.

 The thermoplastic elastomer in accordance with the present invention is aptly suited for uses requiring low density (less than about 20 pcf) and closed cells. These advantageous properties make it particularly suitable for use as industrial gaskets, seals, cushion insoles for shoes, shock pads, elastomeric springs, and appliance foot pads,
15 providing a commercially attractive additions to present materials. These and other features of the invention will become better understood with reference to the following detailed description, drawings, and appended claims.

Detailed Description of the Invention

 In accordance with the present invention, a thermoplastic elastomer resin is
20 foamed using a supercritical fluid under conditions of controlled temperature and pressure drop rate, thereby producing closed-cell, microcellular foams. Such foams may be produced in the form of thin sheets.

 Thermoplastic elastomeric resins suitable for use with the present invention include, but are not limited to those known in the art such as homopolymers,
25 copolymers, and blends of polyolefins, polyurethanes, polyamides, polyesters, metallocene plastomers, and the like. Preferred elastomers include styrenic block copolymers and thermoplastic vulcanizates (i.e., blends of polyolefin and vulcanized rubber). One particularly preferred elastomer is styrene-ethylene butylene-styrene

-3-

(SEBS), which is available under the trade name KRATON from Shell Chemical Corp. Another particularly preferred elastomer is a thermoplastic vulcanizate having a Shore A hardness of 73 or greater, which is commercially available from Advanced Elastomer Systems, Akron, OH under the trademark SANTOPRENE[®]. SANTOPRENE[®] is a
5 blend of polypropylene and ethylene propylene diene (EPDM) copolymer.

Additional components of the foams include, but are not limited to those known in the art, for example nucleating agents, pigments such as carbon black, fire retardants, and/or diffusivity modifiers such as glyceryl monostearate.

The resin or resin mixtures with the above additives are foamed with a tandem
10 extruder using a supercritical fluid as a blowing agent in accordance with the methods described in U.S. Patent No. 5,158,986 to Cha et al., U.S. Patent Application Serial No. 08/692,060, filed August 2, 1996 as a re-issue of U.S. Patent No. 5,334,06 to Balswin, et al., and U.S. Patent Application Serial No. 08/782,955, filed January 13, 1997 to Park et al., all of which are incorporated herein by reference in their entirety. Thus, the
15 polymer and the blowing agent are mixed in the melt stage in the first extruder, and then transferred to the second extruder the temperature and pressure are reduced in order to initiate foaming. The supercritical fluid is preferably carbon dioxide. Alternatively, the polymers and any optional fillers are first melt compounded in high-shear equipment such as a BRABENDER[™] or twin-screw extruder or other suitable
20 equipment at appropriate temperatures (melt temperature being the minimum and the decomposition temperature of the elastomer being the maximum usable limits). The compounding is preferably performed long enough to obtain a homogeneous mixture on a microscopic level, the homogeneity being measured by the thermogravimetric analysis (for example 15 minutes in a BRABENDER[™] and 3 minutes in a twin-screw
25 extruder). This mixture is then mixed with blowing agent as described above.

A number of parameters are important in obtaining the microcellular, closed-cell, low density foams of the present invention, particularly in the form of thin sheets. It has surprisingly been found that obtaining thin sheets of closed cell, microcellular thermoplastic foams depends critically on the melt temperature of the resin and the
30 pressure drop rate across the die. In particular, it has surprisingly been found that an

-4-

increase in the melt temperature of will result in a decrease in the density of the resultant foam. However, the inventors hereof have found that there is a maximum to the temperature increase, such that low density foams are obtained at intermediate temperatures. The preferred melt temperature is in the range of from about 320-360 °F.

5 For thermoplastic vulcanizates such as SANTOPRENE®, the optimal melt temperature is in the range from about 330-360 °F, while for an SEBS such as Kraton, the optimal melt temperature is in the range from about 320-350 °F.

Importantly, the pressure drop rate across the die must be maintained at an intermediate level. Ordinarily, increasing the pressure drop rate across the die (dp/dt)

10 results in a decrease in the density of the obtained foams, as well as very fine cell structure. However, it has been found that the optimal dp/dt has a maximum value that is preferably not exceeded. Thus, higher pressure drop rates in the range from 11-15 GPA (die of 0.042 inches tapered) gives rise to low density foams of about 8 pcf with uniform cell sizes of about 150 microns for the thermoplastic vulcanizate

15 SANTOPRENE® 201-64, and low density foams of about 6 pcf and non-uniform cell size of about 250 microns for Kraton GLS 7715-9. Both foams had very poor mechanical strength.

Lower pressure drop rates in the range from about 0.1 to about 0.8 GPA (die of 0.08 x 1.2 inches) gave rise to higher density foams of about of about 14 pcf with

20 uniform cell sizes of about 150 microns for the thermoplastic vulcanizate SANTOPRENE® 201-64, and low density foams of about 8 pcf and non-uniform cell size of about 250 microns for Kraton GLS 7715-9. Both foams had fairly good mechanical properties.

However, intermediate pressure drop rates in the range from about 0.8 to about

25 2.6 GPa (die of 0.06 x 1.2 inches) gave rise to foams with a density of about of about 12 pcf with uniform cell sizes of about 100 microns for the thermoplastic vulcanizate SANTOPRENE® 201-64 low density foams of about 9 pcf with uniform cell size for SANTOPRENE® 201-73. Intermediate pressure drop rates in the range from about 1.8 to about 4.8 GPa (die of 0.05 x 0.75 inches) gave rise to higher density foams of about

30 12 pcf (un-optimized) and uniform cell size of about 150 microns for Kraton GLS

-5-

7715-9. All of these foams had very good mechanical properties. Accordingly, pressure drop rates in the range from about 0.1 to about 4.8 GPa are preferred in the practice of the present invention, while pressure drop rates in the range from about 0.8 to about 4.8 GPa are most preferred.

5 Other parameters which affect the production and properties of the foams of the present invention include the concentration of the blowing agent (supercritical fluid), which affects the density of the foam. Optimal blowing agent concentration appears to be about 3% by weight of the polymer. Beyond 6%, gas comes out of solution and the polymer cannot support itself. Cooling the foam as it came out of the die resulted in a
10 density reduction of at least about 15%.

Melt strength and viscosity of the foaming composition are other important parameters in successfully producing foam sheets. Melt strength in particular is improved by the addition of one or both of a high molecular weight ethylene propylene diene terpolymer (EPDM) and a low density polyethylene (LDPE). Suitable high
15 molecular weight EPDM terpolymers include but are not limited to those having diene monomers such as dicyclopentadiene, 1,4-hexadiene or ethylidene norbornene. A higher molecular weight elastomer comprising ethylidene norbornene is commercially available under the trade name Royalene 505 from the Uniroyal Chemical Company. Another suitable high molecular weight EPDM is available from Uniroyal under the
20 trade name IM-7100. Suitable LDPE's include those available from under the trade names D4032F from Eastman Chemical Co., DFOB6005 from Union Carbide Corp., and 303AA and 601AA from Westlake Polymers.

The above-described parameters such as melt temperature, melt strength, viscosity, pressure drop rate, and blowing agent concentration may be adjusted as
25 required in order to optimize the density, cell structure and size, compression set, tensile strength and elongation, thickness of a sheet, and skin of the foam. The optimal density is less than about 20 pcf, preferably less than about 15 pcf, more preferably less than about 10 pcf, and most preferably less than about 3 pcf. The optimal sheet thickness in the range of about 0.01 to about 0.08 inches, preferably about 0.015 about
30 0.05 inches. The optimal compression set is less than about 30%, and preferably less

than about 20%. Sheets will be at least about one inch wide, preferably at least about 8 inches wide, more preferably at least about 18 inches wide, even more preferably at least about 24 inches wide, and most preferably at least about 36 inches wide.

The following non-limiting examples further describe the document feed
5 component of the present invention.

Examples

Procedures

Materials were obtained from the sources listed in Table 1 below.

Table 1.

10	Trade Name	Source	Description
	SANTOPRENE® 201-64	American Elastomer	Thermoplastic vulcanizate resin, Shore A = 64
	SANTOPRENE® 201-73	American Elastomer	Thermoplastic vulcanizate resin, Shore A = 73
15	KRATON GLS 7715-9	Shell Chemical Corp.	SEBS resin
	PRO-FAX 6823.	Montell N. Am.	High molecular weight polypropylene
	PRO-FAX 814	Montell N. Am.	High molecular weight polypropylene
	-	Bakaert Corp	Stainless steel filler
20	D4032F	Eastman Chemical	low density polyethylene
	DFOB60005	Union Carbide	low density polyethylene
	303AA	Westlake Polymers	low density polyethylene
25	601AA	Westlake Polymers	low density polyethylene

The following samples (Table 2) were formulated using a tandem extruder having an output rate of 100 lbs/hour, which may be varied by adjustment the revolutions per minute of the screw.

Table 2

Polymer	Head Pressure, psi	Melt Temperature, °F	Blowing Agent, % by weight of polymer	dp/dt, GPA/s	Density, pcf	Average cell diameter, microns	Mechanical properties
SANTOPRENE® 201-64	1420	370	1	0.5	39	80	Good*
SANTOPRENE 201-64	1860	340	1.9	0.7	18	120	Good*
SANTOPRENE 201-64	1340	370	1.9	0.5	22	70	Bad skin
SANTOPRENE 201-64	1040	342	2.9	0.1	16	120	Good*
SANTOPRENE 201-64	1670	331	4.1	0.7	13	120	Good*
SANTOPRENE 201-64	2190	338	3.7	1.1	13	80	Poor****
SANTOPRENE 201-64	2110	352	4.7	12.4	12	20	Good*
SANTOPRENE 201-73	2990	332	2.7	1.4	9	80	Good*
Kraton GLS 7715-9	1560	330	2	0.6	11	250	Good**
Kraton GLS 7715-9	1060	351	2	0.5	17	250	Good**
Kraton GLS 7715-9	1200	322	4	0.5	6	250	Good**
Kraton GLS 7715-9	1550	340	3	7.2	6	250	Poor****
Kraton GLS 7715-9	2140	342	2.6	1.9	10	150	370

*Compression set resistance about 15%, good skin, tensile strength at least about 120 psi, elongation break at least about 60%.

**Compression set resistance about 25-35%, good skin, tensile strength at least about 60 psi, elongation break at least about 70%.

***Compression set resistance about 25-35%, good skin, tensile strength at least about 100 psi, elongation break at least about 330%.

****Elongation break less than about 10%.

In order to optimize viscosity and melt strength, different elastomer blends were prepared in accordance with Table 3 below (parts by weight of the total composition). Viscosity was calculated based on the torque values observed while blending in a Brabender mixer. Overall, blends of SANTOPRENE[®] 201-73 with high molecular weight polypropylene and EPDM had higher viscosities than SANTOPRENE[®] 201-73 alone. Blends of SANTOPRENE[®] 201-73 with high molecular weight polypropylene and EPDM (6:1:3) had higher viscosities than the same components in ratios of 6:2:2. Blends comprising high molecular weight polypropylene (PP 6823) were more viscous than blends comprising high melt strength polypropylene (PP 814).

- 10 Based on the viscosity (and other) results, the compositions set forth in Table 2 were blended and tested for melt strength. In Table 2, S 73 is SANTOPRENE[®] 201-73, S 64 is SANTOPRENE[®] 201-73, PP 6823 is PRO-FAX 6823, PP 814 is PRO-FAX 814, SS is stainless steel filler available from Bakaert Corp., and LDPE is the low density polyethylene having the trade designation D4032F unless otherwise noted.
- 15 Three different tests were used in order to provide an indication of melt strength.

- DMTA (dynamic mechanical thermal analysis) yields the response of a material to a periodic stress at various temperatures (storage modulus), which is directly proportional to elastic modulus. Thus, samples were blended in a Brabender, hot pressed at 380 °F, and allowed to rest for at least 24 hours before testing. Average dimensions of each sample were approximately 20 x 4 x 1 mm. Storage modulus of each sample was measured over the temperature range of 50 to 160 °C using a sweep rate of 5 °C per minute. The advantages of this test are that it is very sensitive to molecular motion and it is conducted across varying temperatures. Generally, as shown in Table 3 below, LDPE blends show low modulus at high temperature, and PP 6823 blends show higher moduli than PP 814 blends. Samples comprising 20% SS fibers show results comparable to those without (data not shown).
- 20
- 25

Tensile tests measure buildup of force (or stress) as the specimen is stretched at a constant rate. It yields force (and thus strength) values, and the results are close to those of the melt test at the melt temperature of the material. Samples having an average size of 0.6 x 0.5 x 0.1 mm were prepared as in the DMTA test, wherein the first
5 value (0.6) is the gauge length. Tensile strength is measured with a Model 1101 Instron using a 100-pound load cell and a cross-head speed of 20 inches per minute at 165 °C. As measured by this test, compositions comprising SANTOPRENE, EPDM and PP 6823 showed higher elongation and toughness. Samples comprising 20% SS fibers show result comparable to those without (data not shown).

10 A near melt extensometer was also used to provide an indication of melt strength (NME). Freshly extruded polymer in the shape of a strand or rod is extended between tow pairs of moving rollers to measure force and elongation at break. Again, compositions comprising SANTOPRENE, EPDM and PP 6823 showed higher elongation and toughness.

15 Results from each of these three tests is presented in Table 3 below.

Table 3.

Resin formulation (ratio)					DMTA (Storage Modulus, MPa)							Tensile		NME		
S 73	S 64	EPDM	PP 6823	PP 814	LDPE	SS	120 °C	130 °C	140 °C	150 °C	160 °C	165 °C	Max. Stress, lb/in ²	Max Strain, %	Max. Stress, lb/in ²	Strain at Break, %
100	--	--	--	--	--	--	9.47	8.10	6.49	4.34	1.83	1.01	110.4	627.8	35	300
80	--	--	--	20	--	--	27.37	23.07	18.43	12.33	3.13	0.77	95.5	1045	29	350
60	--	30	--	10	--	--	8.72	7.51	6.15	4.28	1.99	1.09	--	--	--	--
60	--	30	10	--	--	--	9.25	8.09	6.83	5.30	2.92	1.62	36	1400	50	360
60	--	20	--	20	--	--	16.74	14.51	12.13	8.89	2.86	1.03	--	--	--	--
60	--	20	20	--	--	--	20.84	17.74	14.53	10.66	5.32	2.31	65.5	1600	50	350
80	--	--	20	--	--	--	29.56	24.72	19.58	13.63	5.49	2.08	136	1004	48	310
80	--	20	--	--	--	--	4.38	4.08	3.57	2.90	1.76	1.09	52	813	57	340
--	--	--	--	100	--	--	421.20	301.80	186.00	89.60	9.10	--	--	--	--	--
--	--	--	100	--	--	--	121.80	97.80	73.70	49.20	22.50	14.10	--	--	--	--
--	100	--	--	--	--	--	--	--	--	--	--	--	--	--	33	310
--	60	20	20	--	--	--	18.14	15.32	12.59	9.42	4.46	1.89	78.5	1630	56	345
--	60	20	--	--	20*	--	1.64	1.35	1.18	0.97	0.69	0.59	13	1220	51	378
--	60	20	--	--	20*	--	1.85	1.59	1.37	1.08	0.65	0.59	15.5	602.2	--	--
--	60	20	--	--	20**	--	2.53	2.24	1.90	1.28	0.62	0.55	10.5	360	--	--
--	60	20	--	--	20***	--	1.90	1.67	1.47	1.15	0.66	0.59	11	55	--	--
48	--	16	16	--	--	20	20.29	16.46	12.47	7.97	3.51	2.02	58	1600	65	322

*LDPE having the trade designation DFOB6005

**LDPE having the trade designation 303AA

***LDPE having the trade designation 601AA

-11-

The foamed thermoplastic elastomer in accordance with the present invention is suited for uses requiring low density (less than about 20 pcf) and closed cells. These advantageous properties make it particularly suitable for use as industrial gaskets, seals, cushion insoles for shoes, shock pads, elastomeric springs, and appliance foot pads, providing a commercially attractive additions to present materials.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is understood that the present invention has been described by way of illustrations and not limitation.

10 What is claimed is:

-12-

CLAIM 1. A method of making a thermoplastic elastomeric foam, comprising
mixing a thermoplastic elastomeric composition with a supercritical fluid in a
first extruder at a first temperature and pressure; and
extruding the mixture across a die having a pressure and temperature change to
5 a second temperature and pressure, thereby causing foaming of the thermoplastic
elastomeric composition to form a closed cell, microcellular foamed thermoplastic
elastomer.

CLAIM 2. The method of claim 1, wherein
the thermoplastic elastomeric resin composition is mixed with the supercritical
fluid in a first extruder and then transferred to a second extruder.

CLAIM 3. The method of claim 1, wherein
the thermoplastic elastomeric resin composition is selected from the group
consisting of styrenic copolymers, thermoplastic vulcanizates, styrene-
ethylenebutylene-styrene, and a thermoplastic vulcanizate having a Shore A hardness of
5 at least 73.

CLAIM 4. The method of claim 3, wherein
the melt temperature of the thermoplastic elastomeric resin composition is in the
range from about 320-360 °F.

CLAIM 5. The method of claim 2, wherein
the melt temperature of the styrene-ethylenebutylene-styrene is in the range
from about 320-350 °F, and the melt temperature of the thermoplastic vulcanizate is in
the range from about 330-360 °F.

CLAIM 6. The method of claim 3, wherein
the thermoplastic resin composition further comprises an ethylene propylene
diene, terpolymer, a low density polyethylene, or a combination thereof.

CLAIM 7. The method of claim 1, wherein
the pressure drop rate across the die is in the range from about 0.1 to about 4.8 GPa.

CLAIM 8. The method of claim 1, wherein
the pressure drop rate across the die is in the range from about 0.8 to about 4.8 GPa.

CLAIM 9. The method of claim 1, wherein
the pressure drop rate across the die is in the range from about 1.4 to about 1.4,
and the second temperature is about 330 °C.

CLAIM 10. The method of claim 1 wherein the thermoplastic resin composition is
melt compounded prior to mixing with the supercritical fluid.

CLAIM 11. A method of making a thermoplastic elastomeric foam, comprising
melt compounding a thermoplastic elastomeric resin composition, wherein the
melt temperature of the resin composition is in the range from about 320-360 °F;
mixing the compounded resin composition with a supercritical fluid in a first
5 extruder at a first temperature and pressure; and
adjusting the mixture to a second temperature and pressure, thereby causing
foaming of the thermoplastic elastomeric foam to form a closed cell, microcellular
foamed thermoplastic elastomer, wherein the pressure drop rate across the die is in the
range from about 0.1 to about 4.8 GPa.

CLAIM 12. The method of claim 11, wherein
the pressure drop rate across the die is in the range from about 0.8 to about 4.8 GPa.

CLAIM 13. The method of claim 11, wherein
the thermoplastic elastomeric resin composition is mixed with the supercritical
fluid in a first extruder and then transferred to a second extruder.

CLAIM 14. The method of claim 11, wherein
the thermoplastic elastomeric resin composition is selected from the group
consisting of styrenic copolymers, thermoplastic vulcanizates, styrene-
ethylenebutylene-styrene, and a thermoplastic vulcanizate having a Shore A hardness of
at least 73.

5

CLAIM 15. The method of claim 14, wherein
the thermoplastic resin composition further comprises an ethylene propylene
diene, terpolymer, a low density polyethylene, or a combination thereof.

CLAIM 16. The method of claim 11, wherein the thermoplastic resin composition
further comprises a filler.

CLAIM 17. The method of claim 11, wherein the formed foam is low density and
has closed cells in the microcellular range.

CLAIM 18. A thermoplastic, elastomeric foam manufactured by the method of claim
1.

CLAIM 19. A thermoplastic, elastomeric foam manufactured by the method of claim
11.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/05945

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 14/06, 36/04; C08J 9/04

US CL : 521/79, 142, 146, 148, 150

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 521/79, 142, 146, 148, 150

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,302,624 A (REEDY et al.) 12 April 1994 (12-04-94), see the entire document.	1-19
Y	US 5,422,377 A (AUBERT) 06 June 1995 (06-06-95), see the entire document.	1-19
A	US 5,589,519 A (KNAUS) 31 December 1996 (31-12-96), see the entire document.	1-19

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 JULY 1999

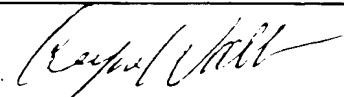
Date of mailing of the international search report

14 JUL 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOHN M. COONEY JR. 
Telephone No. (703) 308-2351